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CHANGES IN PHYSICO-CHEMICAL PROPERTIES OF SOILS FERTILIZED BY AGRO-INDUSTRIAL RESIDUES

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SUMMARY

Cyclic fertilization of two soils by olive oil-mill sludge compost (alpechin) and vinasse, improved their agrotechnical properties. THESE soils were classified as Typic Xeropsamment and Typic Xerorthent. The effect of fertilization was studied by X-ray diffraction, and measurement of water sorption and water retention from gaseous phase. Incorporation of fertilizers increased both water sorption and water retention, especially in case of sandy soil. Relative calcite content in the clay and silt fractions was changed after addition of fertilizer, this distribution was dependent on soil type.

KEYWORDS:

Waste fertilizers; Alpechin; Vinasse; Water sorption and retention.

INTRODUCTION

Crop response to the application of agricultural and agroindustrial waste fertilizers is well documented, however, there are few studies on the effect of such fertilization on soil properties, and the conclusions are sometimes controversial (1,2). Organic fertilizers derived from agricultural and agroindustrial wastes contain significant amounts of organic matter and nutrients, thus they may be used for fertilization or improvement of agricultural soils, either directly or after suitable treatment (3). Humification and mineralization of the wastes can contribute to changes in soil physical and chemical properties favoring nutrition and growth of plants. Thus, soil may be an ideal recycling substrate for many wastes products, based on the physical, chemical and microbiological interaction between the components and microorganism of soils and wastes. After a period of biodegradation soil fertility can be enhanced because of the increase of organic matter and nutrient content (4).

Agricultural use of "alpechín" (wastewater from olive oil production) and vinasse (a liquid by-product from sugar beet industries), both with a high organic matter content, K and Mg, is recognized as an environmentally and economically appropriate method of waste disposal (5). Today, discharging into rivers of these by-products create an increasing pollution problem in many countries (6,7), thus their agricultural utilization may be of vital importance.

Soil fertility is related to soil-water interaction, which is strongly dependent on its specific surface. This value is measured by various methods, usually by sorption of various organic or inorganic molecules. A suitable method to know the soil-water system seems to be the water sorption determination. It may be measured at various relative humidity p_1/p_0 conditions using respective coefficients derived from the "known" number of sorbed water molecule layers. This has been applied in soil mechanics (8) and the comparison with other methods of specific surface measurement indicated consistent results (9,10).

Water sorption was studied here to explain the reason of changes in properties of two soils of different characteristics after their fertilization with two agroresidues. This study was supported by X-ray diffraction tests.

MATERIALS AND METHODS

Two surface soils were used in this work. Soil 1 is classified as Typic Xeropsamment, of sandy texture and medium calcium carbonate content. Soil 2 is a Typic Xerorthent, of loam clay sandy texture and high calcium carbonate content. Some characteristics of these soils are shown in Table 1.

The waste fertilizers used were "alpechin" (A), a composted olive oil mill sludge, and vinasse (V), the by-product at the production of alcohol from sugar beet molasses. The waste fertilizers were applied during three years to containers of 4L capacity, each filled with 6.1 Kg of either one of the two topsoils.

TABLE 1
Selected chemical and physical properties of the soils.

Soil	OM* (%)	pH	CaCO ₃ %	CEC** cmol _c kg ⁻¹	Clay < 2mm %	Silt 2-50mm %	Fine Sand 50-200mm %	Coarse Sand > 200 mm %
1	0.14	8.5	8.6	3.9	7.6	2.5	2.5	87.4
2	0.53	7.9	27.0	9.4	21.3	21.1	12.8	44.8

*Organic matter content. **Cation exchange capacity.

Every year the soils of each container (except the untreated control) were mixed either with 67.8 g of alpechin or with 250ml of vinasse of 5% wt/v dissolved in water. Thereafter, the whole soil samples were air dried, sieved (< 2 mm) and stored at 4°C before further study.

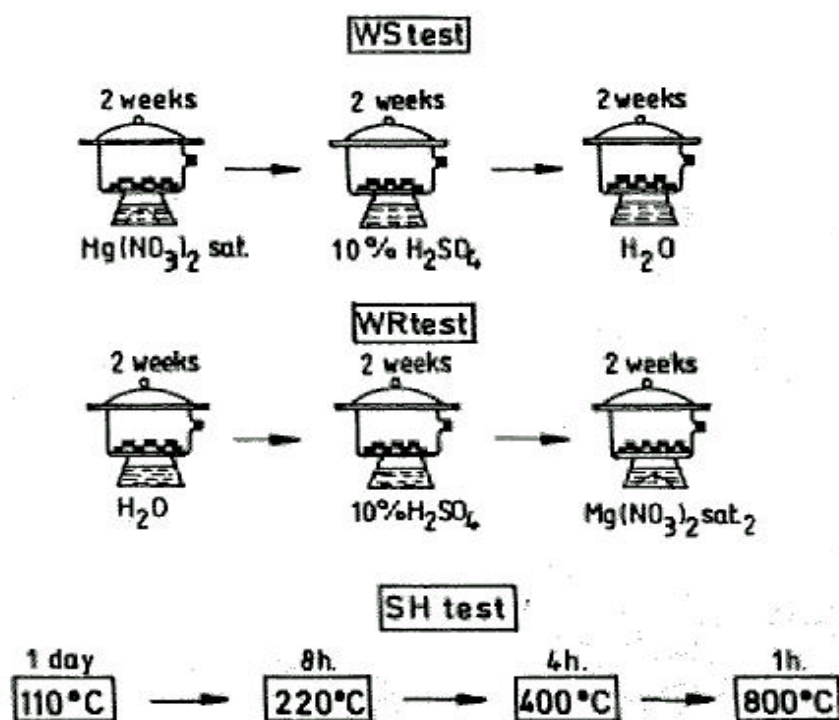
X-ray diffraction (XRD) was used to identify the minerals present (11) in the clay and silt fractions of the soils (separated by suspension), and to find the possible changes after fertilization. X-ray diffraction patterns of powder samples were obtained using a Siemens Kristalloflex D-500 diffractometer with Ni filtered Cu K α radiation.

To estimate the soil-water interactions, water sorption (WS) and water "retention" (WR) were measured as described by Stepkowska (12), and shown in Figure 1. In WS test, 0.5 g of the air dry powder (WS) or of the oven 110°C dry powder (WSo) were put in triplicate in aluminum containers (3 cm x 2 cm x 1 cm) and placed for two

weeks at 30°C and atmospheric pressure, successively in desiccators over solutions producing the following relative water vapor pressures (p/p_0): 0.5 (over the saturated Mg(NO₃)₂ solution), 0.95 (over the 10% H₂SO₄ solution) and 1.0 (over distilled water). After finishing WS test, the WR test is carried out in the same samples. In WR test the relative humidity was decreasing successively in an analogous way. In this work different water vapor pressures were used to measure water sorption and retention.

At the relative water vapor pressure $p/p_0 = 1.0$ ($p = 0.023$ bar at 20 °C and 0.042 bar at 30 °C) the soil water suction (soil potential) was 10.2 cm, pF about 1. At $p/p_0 = 0.99$ the soil suction is 6.1 cm, $pF > 3$ (13). At these conditions water is sorbed or retained on the surfaces of particles within clusters and aggregates (in micropores): at $p/p_0 = 0.5$ in bimolecular layer, and at $p/p_0 = 1$ up to four-molecular layer (8,14). At $p/p_0 = 1.0$ the capillary condensation may occur in mesopore and in macropores (15).

FIGURE 1
Water sorption (WS) and retention (WR) and stating heating (SH)



RESULTS AND DISCUSSION

Smectite dominates in the clay fraction of soil 1 (Fig. 2a). The peak at 15.31 Å of high intensity and no broadening to either side indicates a good crystallinity. The remaining peaks are low and broad, except that at 4.48 Å (corresponding to 0,20 peak of dioctahedral clay minerals). Addition of A and V caused a slight decrease of the smectite peak intensity at 15.31 Å (Fig. 2 b,c), so that, the remaining peaks were better discernible: illite at 10.04, 5.04 and 3.34 Å, kaolinite at 7.13 Å, calcite peak at 3.04 Å and quartz at 4.26 and 3.34 Å. Calcite peak was very low and broad in the clay fraction of untreated sample (Fig. 2a), and also in the soil treated with V (Fig. 2c).

The silt fraction of soil 1 (figure not shown) contained also an appreciable amount of smectite; the peaks of illite at 10.04 and 5.04 Å were very small. The strongest peaks belonged to quartz (at 4.28 and 3.35 Å) and calcite (3.04 Å). Some feldspar was discernible at 3.20 and 2.13 Å. In this silt fraction after addition of fertilizers, the ratio of peak intensity at 4.48 Å to the intensities of d_{001} peaks, increased as compared with the untreated sample, indicating more random particle orientation.

Calcite content was higher in both fertilized samples, especially in silt fraction of the soil amended with A (data not shown). Thus the addition of both fertilizers to soil 1 caused an increase in calcite content in the silt fraction, whereas only alpechin addition caused it in the clay fraction, resulting in clay particle cementation. There is also a more random orientation of clay minerals in the silt fraction after fertilization, which was the reason for the decreasing of the peak intensity ratio at 4.48 Å to the d_{001} peaks. The XRD diagrams of the clay fraction of soil 2 showed the presence of smectite, illite and kaolinite, the first two mainly in mixed layers. The peaks are low and broad (Fig. 3a). Strong calcite peaks were detected in the original sample. The intensities of calcite peaks (3.04, 3.84, 2.49, 2.28 and 2.09) became lower after treatment with A (Fig. 3b), and after treatment with V they disappeared completely (Fig. 3c).

Thus, the addition of fertilizers to this soil removed the carbonates from the clay fraction (partly by A addition, completely by V addition). Therefore, the intensities of the remaining peaks apparently increased. Silt fraction behaves differently, since calcite peaks are present in all the samples of soil 2 (data not shown).

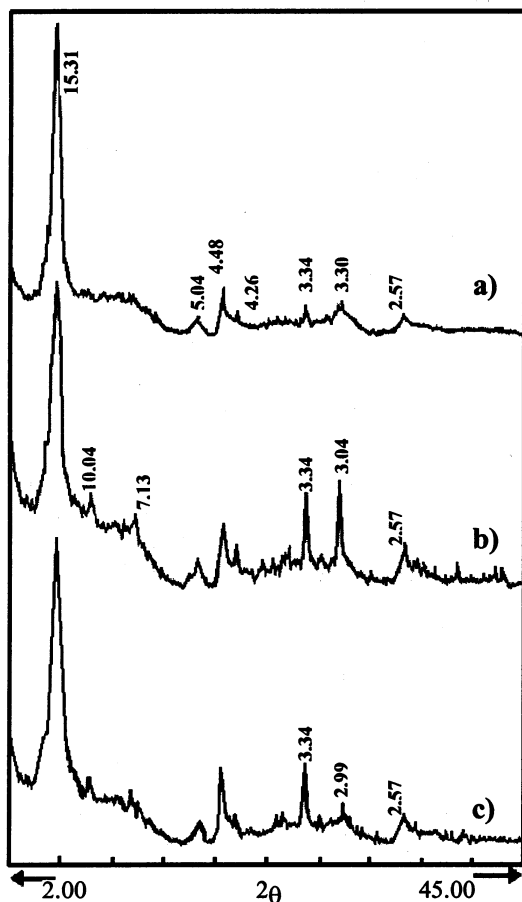


FIGURE 2 - XRD of clay soil 1: a) untreated; b) treated with A; c) treated with V

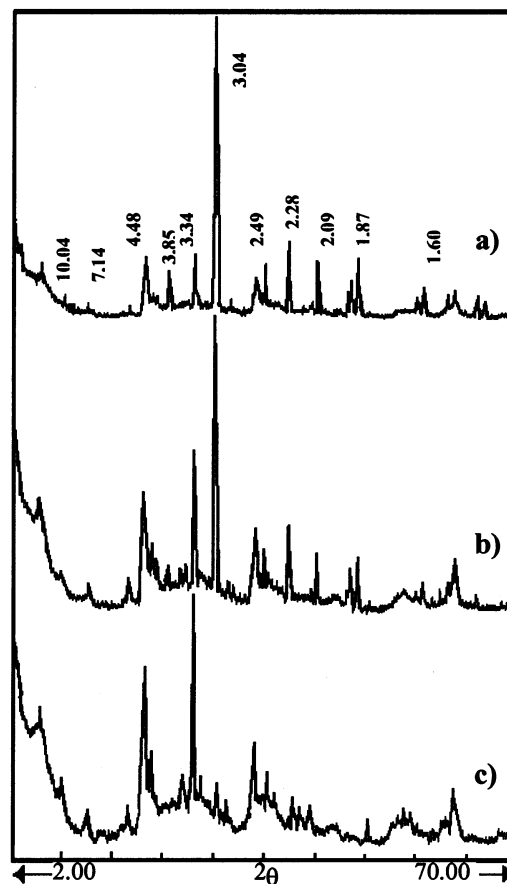


FIGURE 3 - XRD of clay soil 1: a) untreated; b) treated with A; c) treated with V

Water sorption, water retention

A change in WS and WR values at $p/p_0 = 0.5$ and 0.95 indicates the change in specific surface, to which they are proportional, being inversely proportional to particle thickness (14). A change in WS and WR values at $p/p_0 = 1.0$ indicates also a change in specific surface and possibly in macropore water content (16). If these values are higher than twice the values measured at $p/p_0 = 0.5$, this indicates either particle delamination by water sorption or macropore water formed by capillary condensation (17). A large increase in WSo (water sorption after oven drying) as compared to WS (after air drying) indicates a disturbance of cementing bonds between clay particles (14).

The results of WS, WSo and WR tests of the soils with and without waste fertilizers are shown in Table 2. All the WS and WR values of untreated soils are in accordance with the clay fraction content: 21.3% and 7.6% for soils 2, and 1, respectively (Table 1). Indeed: WS and WR of soil 2 \gg WS and WR of soil 1. Thus WS and WR are approximately proportional to the clay fraction content, which is logical: the particles in clay fraction present the highest specific surface.

When waste fertilizers are applied to soil, the organic matter input may influence water sorption and water retention in the following ways: direct effect due to organic particles themselves, which have a high water sorption capacity (18).

Organic molecules may intercalate in the interlayer space of clay particle facilitating the particle delamination. An indirect effect due to the modification of other physical properties: bulk density, porosity, pore size distribution, etc. (2).

The addition of A and V caused an increase in water sorption (WS) and water retention (WR) at most of the p/p_0 conditions, indicating a change in specific surface. This increase is especially pronounced at the saturated water vapor pressure ($p/p_0=1$), indicating either an increased meso- and macro-pore water content (16) or further increase in specific surface due to water sorption (particle delamination).

The relative increase in WS and WR of the soils with the addition of fertilizers is the highest in soil 1, which has a low clay fraction (7.6%) and high sand content (89.9%). Tester (18) indicated that this improvement seems to be related to the decrease in bulk density of soils with coarse texture. This behavior normally occurs in soils with a clay fraction content lower than 15% (19).

In soil 2 at $p/p_0=1$ somewhat higher WS and WR were observed after fertilization, but they were more noteworthy after V addition. This can be connected with the complete disappearance of calcite from the clay fraction, so, the cementing bonds are removed and, consequently, the water sorption increases. In general, at any p/p_0 value the addition of vinasse caused a higher increase in water sorption (WS) than alpechin addition, in both soils. That is particularly noteworthy for $p/p_0=1$.

TABLE 2
Water sorption (WS) and water retention (WR) of air dried soils, and water sorption of soils dried at 110°C (WSo) (in weight percent), without and with fertilizers, at the given p/p_0 .

Soil	Test	W at p/p_0			Soil	Test	W at p/p_0		
		0.5	0.95	1.0			0.5	0.95	1.0
1	WS	0.8	1.2	1.0	2	WS	1.7	2.6	4.4
	WR	0.8	1.2	1.7		WR	2.0	3.2	3.5
	WSo	0.6	1.2	0.8		WSo	1.7	2.7	5.3
1 A	WS	1.0	1.7	4.0	2 A	WS	1.9	2.8	3.9
	WR	0.9	1.8	2.6		WR	1.8	3.2	4.6
	WSo	0.9	1.4	6.7		WSo	1.8	3.3	4.0
1 V	WS	1.1	1.8	6.2	2V	WS	1.9	3.2	7.0
	WR	0.9	1.9	6.7		WR	1.8	3.7	7.5
	WSo	0.9	1.6	4.9		WSo	1.7	4.0	10.9

Mean values of three determinations. Standard deviation ranged between 0.1 and 0.3 %, except for WSo at $p/p_0 = 1.0$ of soil 2, where it was about 1 %.

CONCLUSIONS

The addition of waste fertilizers (alpechin and vinasse) caused a change in the organic matter content and in the carbonate distribution into particular size fractions (clay and silt).

The incorporation of alpechin and vinasse increased soil water retention at $p/p_0 = 1$ in the two soils. At $p/p_0 = 0.95$ it increased in soil 1 only, and at $p/p_0 = 0.5$ the WR was not affected by the addition of fertilizers, though water sorption (WS) increased in all the cases. This indicates clay particle delamination at the more elevated p/p_0 due to addition of fertilizers.

The transfer of calcite to the finer fractions of soil 1 created contact bonds between clay particles, what impeded water escape from the laminar structure (some water evaporated above 110°C). These contact bonds were destroyed on drying at 110°C, and these samples, in general, sorbed more water than the air-dry ones. The addition of fertilizers to soil 2, which presents initially a high carbonate content in the clay fraction, caused its decrease with A and its complete disappearance in the clay fraction with V addition, accompanied by destroying of contact bonds, so the WS_0 was higher than WS (specially for V). No important changes in the carbonate content of the whole soil occurred, since the change in weight loss between 400 and 800°C did not exceed the standard deviation.

The simple water sorption test and measurement of weight loss on static heating supplied interesting information on the change in soil properties upon fertilizer addition, which was confirmed by XRD study. Thus these methods may be used for evaluation of the agro-residues as fertilizer of a given soil. The time dedicated to this evaluation may be shortened drastically.

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